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ABSTRACT

New, high performance reverse osmosis membranes experience a troublesome rate of fouling by colloidal and dissolved constituents in feedwaters. In field tests on nonbrackish surface waters, for instance, the U.S. Army Mobility Equipment R&D Command (MERADCOM) has observed performance declines in spiral wrap membrane modules that limit their useful life to three months. This problem is not experienced only by MERADCOM but occurs to varying degrees throughout the water treatment industry where reverse osmosis processes are used. The purpose of this research program is to investigate the incipient fouling mechanisms taking place on membrane surfaces, characterize the foulant deposits, and search for practical means to retard or eliminate the membrane fouling process. Naturally occurring surface waters were to be used in these tests because of the difficulty in simulating naturally occurring foulants.

Clays and inorganic colloids are easily removed from feedstreams by polymeric flocculation and sand filtration processes. The residual organic colloids in the feedwater presumably consist of humic acids (major) and a variety of other organic materials (minor), depending on the water source. These organic colloids are present in relatively small amounts of about 10 to 25 ppm, and would be difficult to remove compared with the inorganic colloids. Results during the first six months of this program showed that organic materials played a principal role as membrane foulants in all cases. Foulant deposits on membranes (obtained from MERADCOM) that had been exposed to Potomac River water feed and to seawater feed streams were characterized by surface analysis techniques. These included ESCA (electron spectroscopy for chemical analysis), AES (Auger electron spectroscopy) and scanning electron microscopy. Elemental analyses via ESCA and AES showed that carbon, oxygen, and nitrogen constituted over 70 percent of the foulant coating on membranes exposed to Potomac River water, for instance, and were nearly as high in the seawater foulants. The minor inorganic constituents were mostly clay and iron hydroxides for both the river and seawater with lesser amounts of other heavy metal salts. Thus, organic compounds rather than inorganic scale was the major cause for the fouling of membrane surfaces.

Three approaches chosen to reduce membrane fouling were as follows. The first approach was to improve the pretreatment of the feedwater to remove more of the organic colloids. The second approach involved addition of cationic polymers such as polyethylenimine (PEI) to the feedwater. The organic colloids were complexed by (PEI) reducing the fouling rate. Third, attempts were made to modify the surface of the membrane to decrease the adhesion of the foulant. The latter two approaches were difficult to control, so that most efforts have been concentrated on methods to remove organic colloids before the feedwater contacts the membrane.

The pretreatment process used by MERADCOM involves addition of an organic polymer flocculating agent followed by sand filtration. The flocculant is a positively charged polymer containing quaternary amine groups. When used with Potomac river water this cationic polymer was reported to act nearly stoichiometrically

to flocculate the negatively charged inorganic and organic colloids. In the case of Mississippi river water which contains a high organic content and less clay this flocculant produced a loosely aggregated floc visible mostly as an increase in turbidity. If not removed effectively in the filtration step, this floc fouled the membranes faster than if no flocculant was used. Other commercial flocculants were evaluated but none had any advantage over the type now used by MERADCOM.

Alum and ferric chloride are coagulating agents for water treatment that are frequently used alone or in conjunction with the organic polymer flocculants. It is known that aluminum and iron salts in an acid pH range exist as polymeric hydroxides with a positive charge and are effective for flocculating the organic colloids in water. We have found that ferric chloride is somewhat better than alum for removing the organic colloids from river water. But of more importance, however, was the fact that alum residues fouled the membrane whereas ferric chloride residues did not.

As a result of these observations on the effect of ferric chloride we have developed a process for pretreatment of river water that eliminated fouling flux decline in our accelerated test. In this process raw river water was treated with 10 ppm of chlorine and 10 to 50 ppm of ferric chloride. The pH of the water was adjusted to 5.5 with sulfamic acid and filtered to give a turbidity of less than 1 FTU. In addition to adjusting the pH into the optimum range, the sulfamic acid complexed the chlorine so that it did not oxidize the membrane. Also, excess ferric ions were chelated by the sulfamic acid so that the ferric oxide sols would not excessively reduce the filtration cycles of the sand filters.

The results of this research program are to be submitted for publication in the form of two papers. The first entitled, "Surface Analysis of Foulant Deposits on Reverse Osmosis Membranes" will cover the ESCA analysis work. The second paper is entitled, "Control of Membrane Fouling in Military Field Reverse Osmosis Systems" and deals with practical approaches for coping with the MERADCOM fouling problem.

